Summary

Eyesight is one of the most powerful senses we have. With our eyes we can, quite sensitively, detect certain interactions between matter and visible electro-magnetic waves. For example we can distinguish differently colored materials that absorb different parts of the visible spectrum. We can even detect materials having no appreciable absorption of the visible spectrum. Polished metals for instance, reflect the visible light and appear shiny and non-transparent. Well-cut diamonds on the other hand, reflect visible light under certain angles while being transparent under other angles.

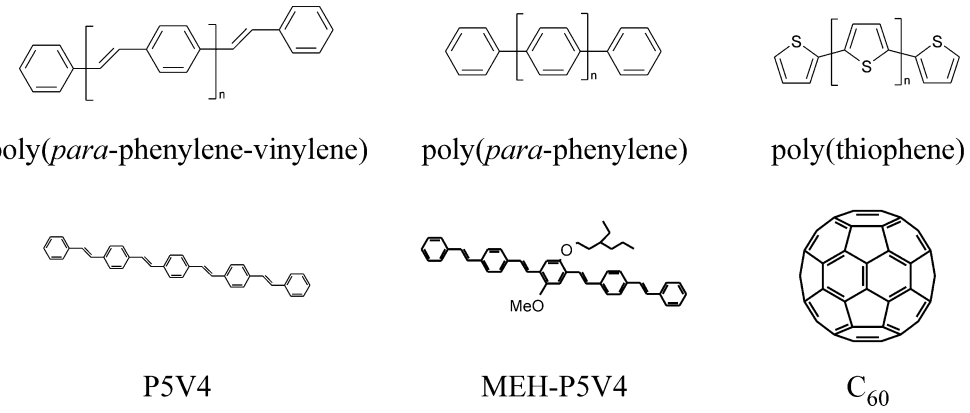
Whether light is absorbed depends on the details of the electronic structure of the material. If one can alter the electronic structure of a material one may thus be able to alter the appearance of the material. The paint industry for example uses the knowledge of material scientists, such as chemists, to develop new paints with appealing colors. One way to alter the electronic structure of a material is by changing the chemical structure, thereby creating a different material, with different (optical) properties.

Absorption of light is most often associated with a transition in which an electron in the material is excited from an occupied level (often the valence band) to a higher lying unoccupied level (often a level in the conduction band). The thus created excited state may relax to the initial state in several ways. The excited state may cause vibrations in the material. Such vibrations lead to so-called ‘radiationless decay’, in which all or part of the energy difference between the excited state and the ground state is transferred into heat. In fluorescent materials, the excited state relaxes (in part) towards the ground state under the emission of a photon. Again, the electronic structure of the material influences the importance of the different decay paths.

In photovoltaic materials, the electron occupying a level in the conduction band does not necessarily recombine with the now unoccupied level in the valence band, also referred to as ‘hole’. In stead, both charges (electron and hole) may be more or less free to move and wander away from each other (under the influence of an electric field). The opposite charges may be collected by electrodes. Contrary, in electro-luminescent materials, electrons and holes are injected into the electro-luminescent material where they may recombine to form an excited state that decays radiatively.

Electro-luminescent materials as well as photovoltaic materials are often associated with inorganic semicondutors such as Si and GaAs. However, in the 1960’s one found that certain molecular systems such as the acenes revealed properties similar to the inorganic semiconductors. In the 1970’s and 1980’s researchers found that the conductivity of certain

polymeric systems could be changed over the full range from insulator to metal by chemical doping. The polymeric systems consisted of long carbon chains in which single and double carbon-carbon bounds alternate (conjugated polymers). Several examples of conjugated polymers are presented in the top row of figure 1.



poly(*para*-phenylene-vinylene) poly(*para*-phenylene) poly(thiophene)

P5V4 MEH-P5V4 C_{60}

Figure 1 *Several conjugated polymers (top row) and conjugated oligomers (first two molecules of the second row). C_{60} is a molecule with a relatively low (and degenerate) lowest unoccupied molecular orbital, making the material a good electron acceptor. All these molecules are described (to some extent) in this thesis.*

In 1990 Burroughes and collaborators reported the fabrication of 'light-emitting diodes based on conjugated polymers'. Only a few years later, the first photovoltaic cells based on bulk hetero-junctions of conjugated polymers were reported. Soon other typical semiconductor devices were also prepared such as the field effect transistor and (optically) pumped lasers. In order to understand these devices it is important to study the electronic structure of these organic semiconductors. This thesis is devoted to such studies.

More specifically, the studies reported here may be summarized as an investigation in the electronic structure of several conjugated molecules, and how the molecular environment influences the electronic structure of these molecules. The results of these studies may provide a better understanding of these materials and are relevant for several applications such as conjugated polymer based light emitting diodes and photovoltaic devices consisting of blends of conjugated polymers with C_{60}-derivatives.

After the introductory chapter (chapter 1), chapter 2 gives a brief description of the technique to probe the electronic structure of these molecules (photoelectron spectroscopy, PES). Further two set-ups are described that were used to collect the PES data.

In chapter 3 the electronic structure is reported of a series of fragments of the conjugated polymer poly(*para*-phenylenevinylene). We choose to measure these molecules in the gas phase to find the electronic structure of isolated molecules, in absence of any intermolecular interactions. The fragments used for this study have up to five benzene rings. A simple model, which was previously applied to polythiophene and the related oligomers, is used to discuss the low energy electronic excitations in these oligomers. The model is based on a Hubbard-like model. A good initial guess for the parameters of this simple tight-binding model can be obtained from experimental data. After a fitting procedure, the experimentally reported values for the low electronic excitations are accurately reproduced.

It is interesting that this simple model may be applied to both homo-polymeric systems such as polythiophene and poly-*para*-phenylene as well as to alternating copolymer such as poly(*para*-phenylenevinylene). It is found that the bridging group in the copolymer (here a vinylene moiety) acts as a guide for the interaction between the (delocalized) phenyl-like orbitals. The effect of this bridging group is a modification of the model parameters, a detailed description of the electronic structure of the vinylene bridging group is not necessary in this model.

Chapter 4 forms a link between the PES measurements on isolated molecules in chapter 3 and the PES measurements on thin films of these ‘oligo(*para*-phenylenevinyl-enes) reported in chapter 5. In chapter 4, the structure of thin films of P5V4 (see figure 1) vacuum deposited on several substrates is described. The films are typically polycrystalline with small crystallites. The interaction between the oligomers in the thin films seems rather weak: the rather large intermolecular distance indicates only weak Van der Waals-like intermolecular interactions. We therefore expect that the electronic structure of thin films of P5V4 will be very similar to the electronic structure of isolated P5V4 molecules. Except of course that aspect which involves the transfer of electrons and holes between the oligomers.

In chapter 5 the PES measurements on thin films of P5V4 are compared to the PES measurements on isolated P5V4 molecules. Except for a shift in the spectra due to screening effects the electronic structure of P5V4 retains mostly its molecular orbital structure, as expected. Interestingly, we found that at interfaces between metals and conjugated molecules (PPV-like oligomers and C_{60}) that the vacuum levels do not align. The misalignment is caused by an electric field at the interface. The misalignment of the vacuum levels is expected to influence charge transfer processes across metal/organic and organic/organic interfaces, thereby possibly affecting the electrical characteristics of organic semiconductor devices, which contain similar interfaces.

Finally, in chapter six, preliminary results are presented on combined PES and current-voltage (*I-V*) measurements. Ultimately, these measurements enable a one-to-one

comparison between the electronic structure of an *in-situ* prepared device measured by PES, with the *I-V* characteristics of the same device.

Figure 2 shows prototypes of conjugated polymers in polymer light emitting diodes (pLEDs) and photovoltaic devices (PVDs). The structure of these devices is schematically depicted in the middle of figure 2. Both types of devices consist of an organic layer sandwiched between two electrodes. For pLEDs the polymer layer may be a single or double layer; in PVDs the organic layer is most often a blend of electron donor and acceptor like molecules. For example blends of poly(*para*-phenylenevinylene) and C_{60} form so-called 'bulk heterojunction organic photovoltaic cells'. At the bottom of figure 2 typical energy diagrams of these devices are presented.

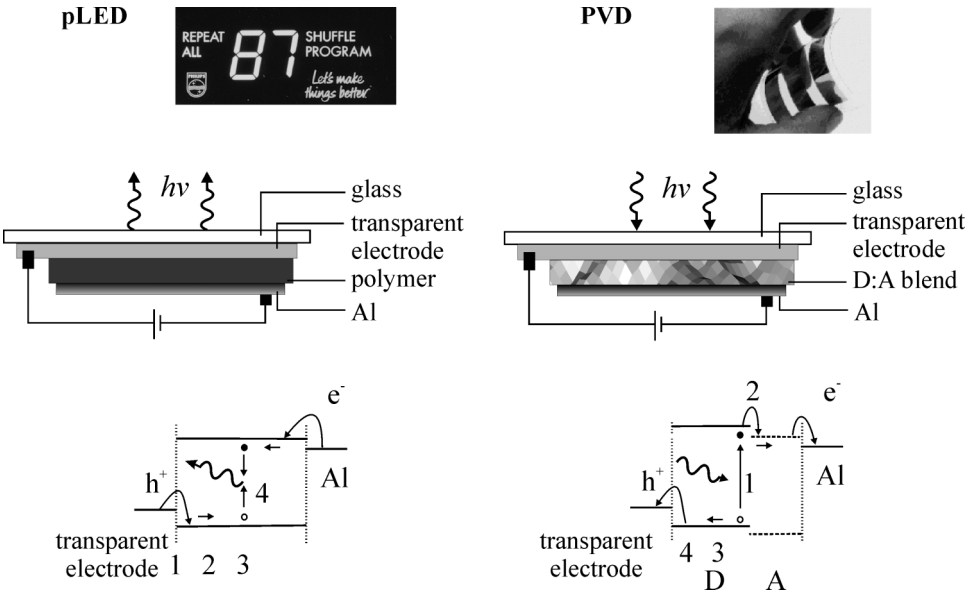


Figure 2 *Examples of prototypes of polymer based pLEDs and photovoltaic cells (top row). The structure of these devices is schematically shown in the middle of the figure. Al stands for aluminum electrode, for pLEDs one also uses calcium electrodes; D:A blend stands for electron donor : electron acceptor blend. In typical devices the electron donor is a conjugated polymer such as a dialkoxy-substituted poly(*para*-phenylenevinylene) and a C_{60}-derivative as electron acceptor. Typical energy diagrams of these devices are presented at the lower part of the figure. The numbers indicate the sequence of steps under device operation. For pLEDs: 1) charge injection, 2) charge transport, 3) charge recombination and exciton formation, and 4) decay of the exciton under the emission of a photon. For a PVD: 1) light adsorption, 2) exciton dissociation (at donor/acceptor interface), 3) charge transport and 4) charge collection at the electrodes.*

The findings in chapter 3 relate the optical properties of pLEDs and PVDs to the chemical structure, for example the length of the oligomer, or the presence of side-chains. The charge transport process is influenced by the intermolecular interactions in the thin film. The weak intermolecular interactions and small crystallites reported in chapter 4 may give rise to a hopping-like transport in which disorder plays an important role. The energy level alignment at interfaces as reported in chapter 5 is important for the charge injection and collection in pLEDs and PVDs respectively. Note that the possible presence of electric fields at the donor/acceptor interface may influence the charge separation process in PVDs. In chapter 6 initial results on complete devices are reported. These measurements may link the PES measurements with the current-voltage measurements on these samples.